

## Supporting Information

### Solvation Shell of the Nitrite Ion in Water: An Ab Initio Molecular Dynamics Study

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# 1 Decomposition of the Distal Region into Two Sub-regions

In Fig.S1, we have shown further decomposition of the hydration shell into three regions: Proximal region as defined above, distal1 region encompassing the space from  $60^\circ$  to  $120^\circ$  and the distal2 region that encompasses the space from  $120^\circ$  to  $180^\circ$  from the axis of the cone as defined in the main text. We note that the distal1 region can also be referred to as the medial region.

The N-O RDFs for these three regions are shown in Fig.S2. We have further decomposed the distal1 and distal2 regions into those of angular thickness of  $30^\circ$  from the axis of the cone and have shown the corresponding N-O RDFs in Fig.S3. It can be seen from these figures of finer conical resolutions that while the proximal water gives rise to the peak at  $2.8\text{\AA}$  in the N-O RDF, water in both distal1 and distal2 regions contribute to the peak at  $3.5\text{\AA}$ . It can also be seen from the results of Figs.S2 and S3 that the broad peak at  $4.5\text{\AA}$  of the N-O RDF captures contributions primarily from proximal and distal1 water in the solvation shell. The water molecules also produce a small peak at  $5.87\text{\AA}$  in the distal2 region as evident from Figs. S2 and S3. These water molecules are in the second solvation shell of the nitrite ion in the distal region. The average numbers of water molecules are calculated by integrating the RDFs of Figs.S2 and S3 up to locations of their first minimum. It is found that, on average, the distal1 region contains 3.3 water molecules which is higher than the 2.4 water molecules present in the distal2 region. Thus, in the overall solvation shell of the nitrite ion, the number of distal1 water molecules is higher than the number of waters in the distal2 region of the solvation shell. The different amplitudes of the distal1 and distal2 RDFs in Fig.S2 could be attributed to the presence of this unequal number of water molecules in the distal1 and distal2 regions around the nitrite ion. Clearly, the decomposition of the RDFs into different conical regions unfolds better the asymmetric hydration behavior of the nitrite ion.

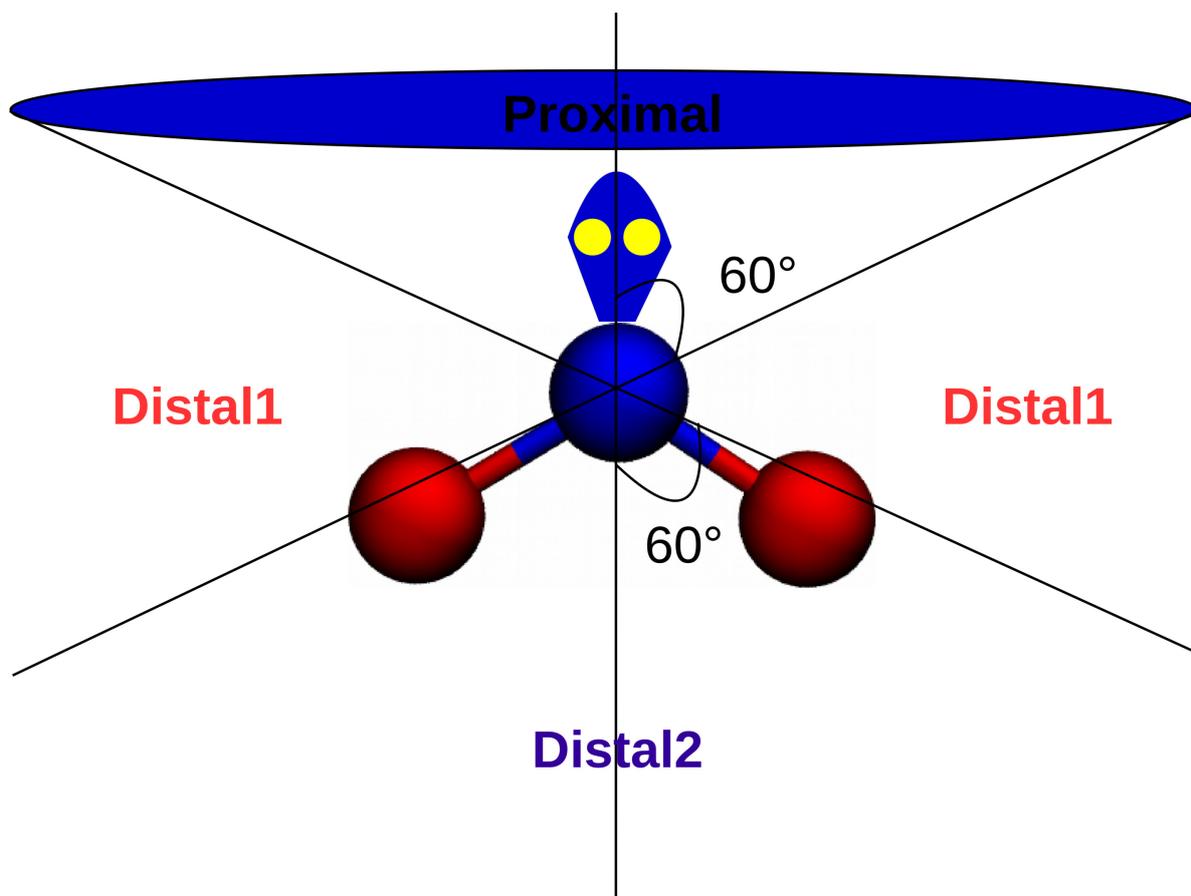


Fig.S1. Definition of proximal, distal1 and distal2 regions of the conical shells around the nitrite ion. The angle  $\theta$  is the conical angle with the principal axis of  $C_2$  symmetry of the nitrite ion. Note that the distal1 and distal2 regions are together defined as the distal region in Fig.2 of the main text.

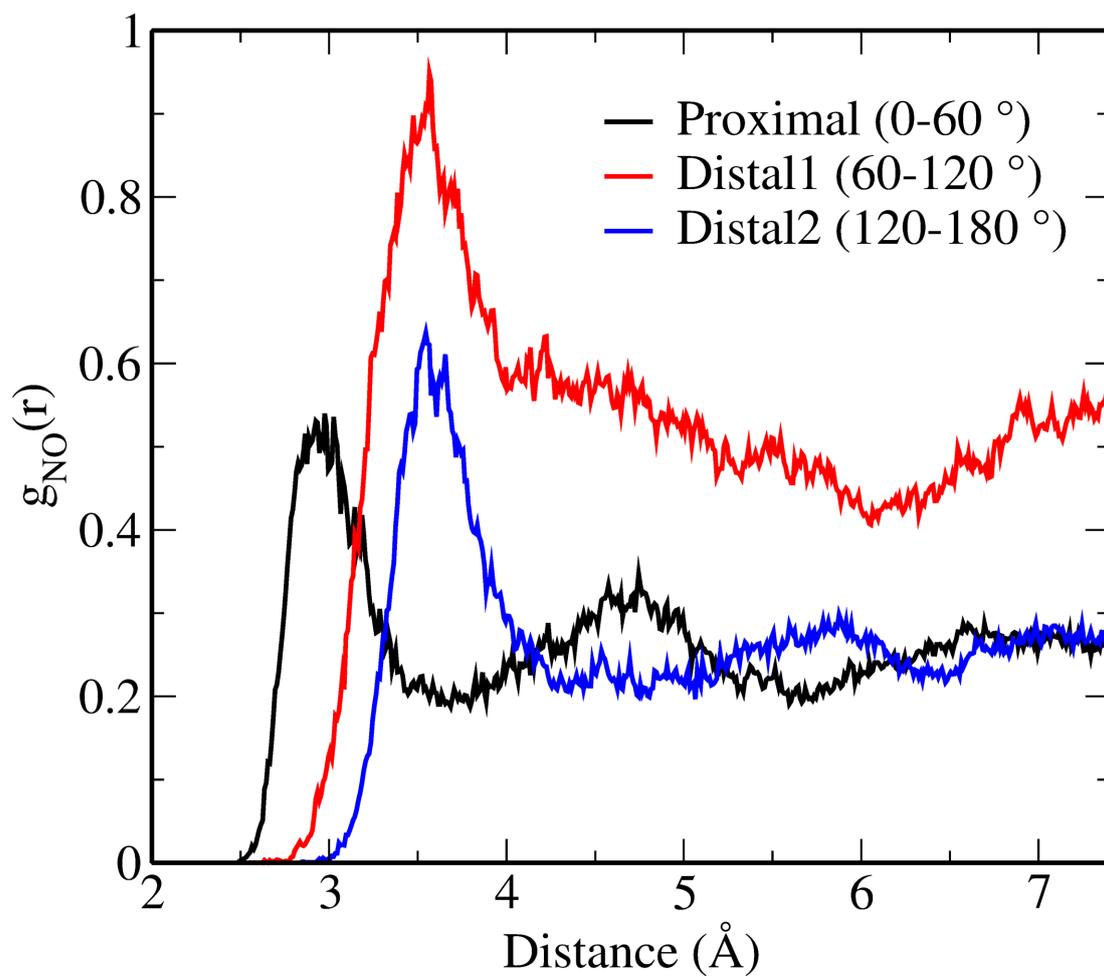


Fig.S2. Radial distribution functions (RDFs) between N of the nitrite ion and oxygen atoms of water (O) are plotted for proximal, distal1 and distal2 regions.

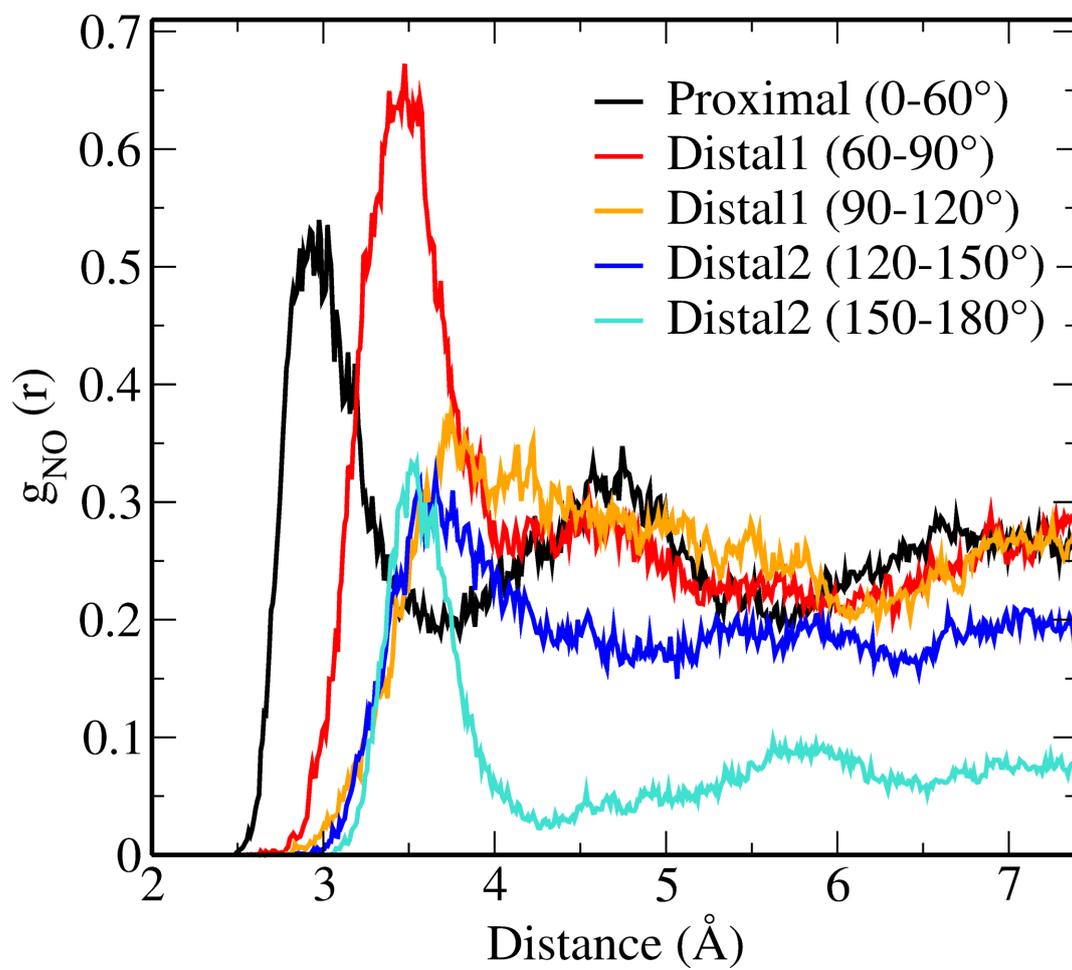


Fig.S3. Radial distribution functions (RDFs) between N of the nitrite ion and oxygen atoms of water (O) are plotted for proximal, distal1 and distal2 regions where the distal1 and distal2 regions are further sub-divided into two regions, each with an angular thickness of 30°.

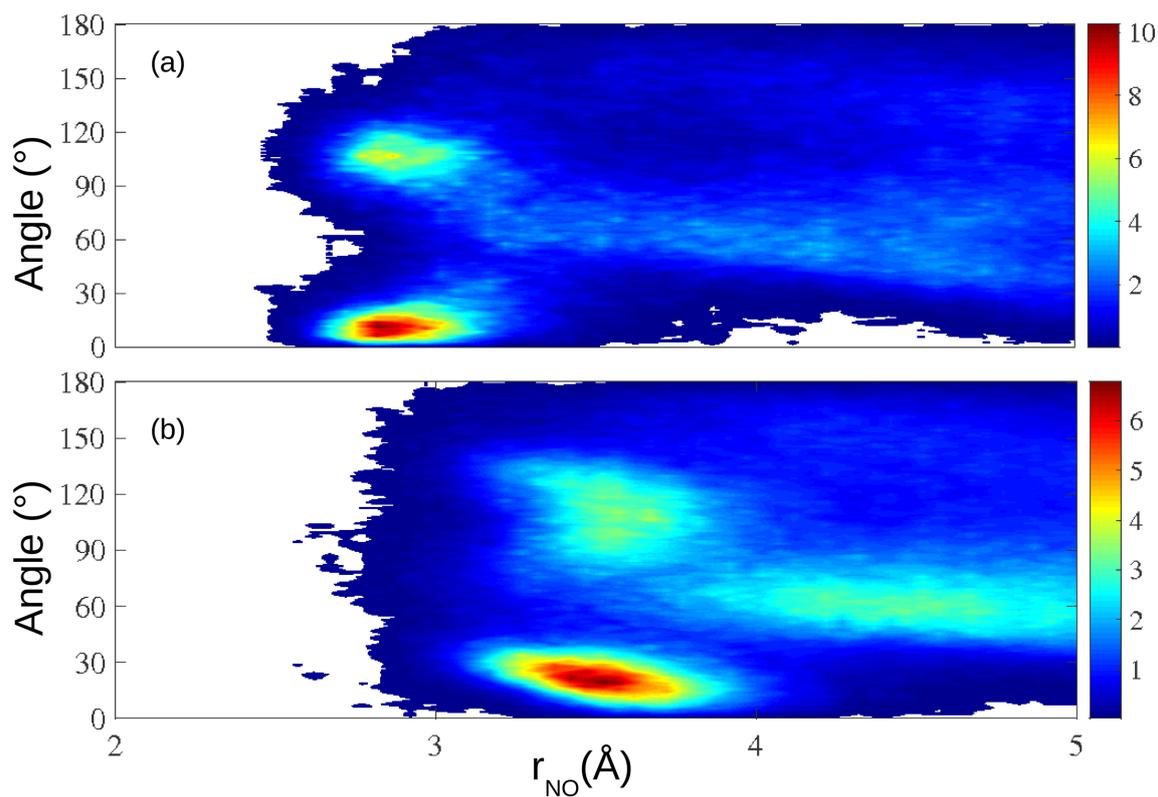


Fig.S4. Contour plots of the hydrogen bond angle vs distance. The x-axis represents the N-O distance in  $\text{\AA}$  and the y-axis represents the hydrogen bond angle originated from two vectors of O-D and O-N. The results of (a) are for the proximal water and those of (b) are for distal water where the proximal and distal regions are as defined in Fig.2 of the main text.

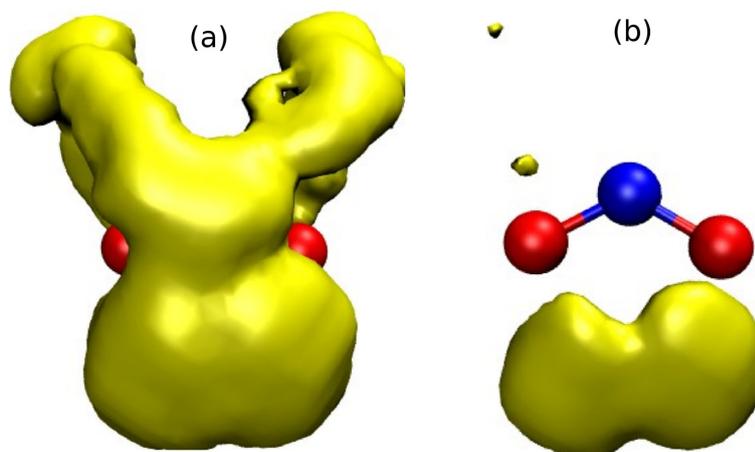


Fig.S5. Spatial distribution functions of deuterium atoms of water around the  $\text{NO}_2^-$  for two isosurface cut-offs of (a)  $5 \text{ nm}^{-3}$  and (b)  $30 \text{ nm}^{-3}$ . Only those D atoms have been considered which are in the range of 2.3-2.7  $\text{\AA}$  from N and, at the same time, 2.3-2.7  $\text{\AA}$  away from any of the two oxygens ( $\text{O}_n$ ) of  $\text{NO}_2^-$ .

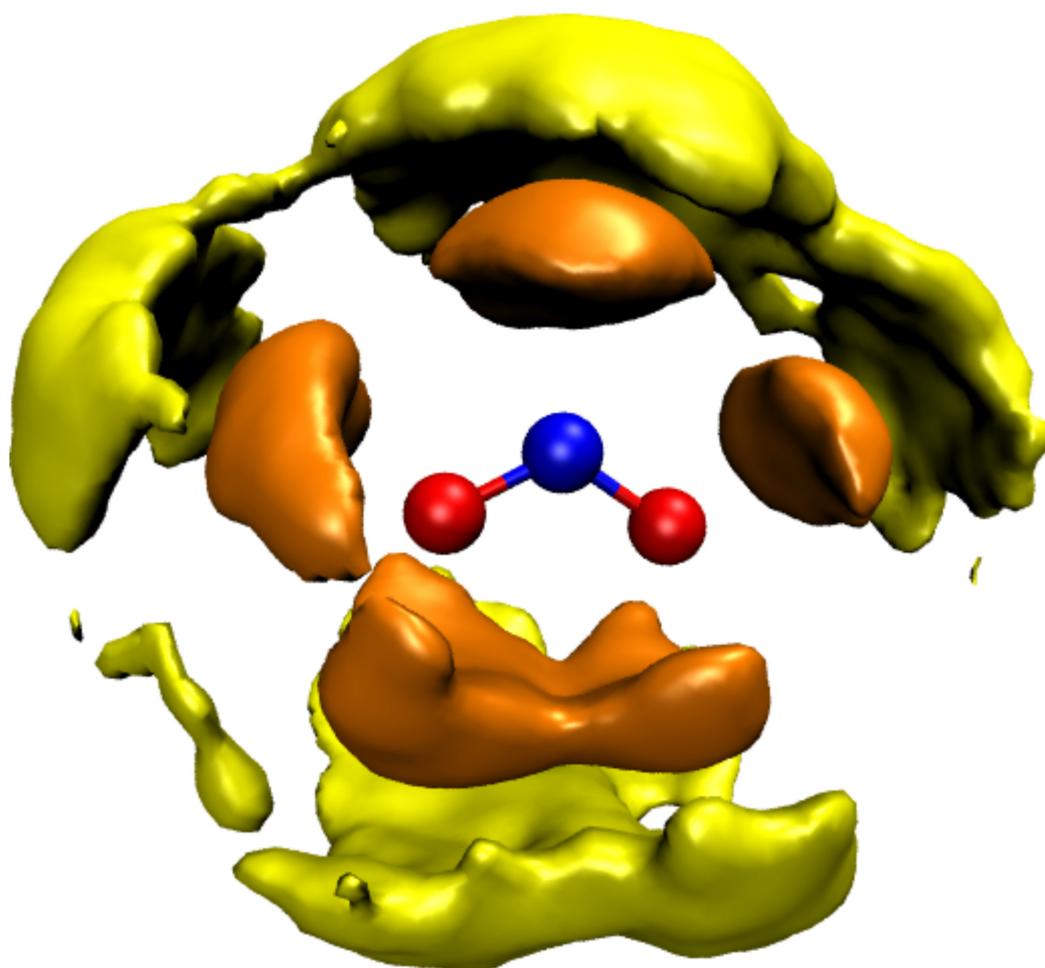


Fig.S6. Spatial distribution functions of first and second deuterium atoms of hydration shell water in the Cartesian space. The orange and yellow colored lobes are for deuterium atoms D1 and D2, where D1 means D atoms that are H-bonded to  $\text{NO}_2^-$  and D2 means the second D atoms of the same  $\text{D}_2\text{O}$  molecules irrespective of whether they are hydrogen bonded to  $\text{NO}_2^-$  or not.

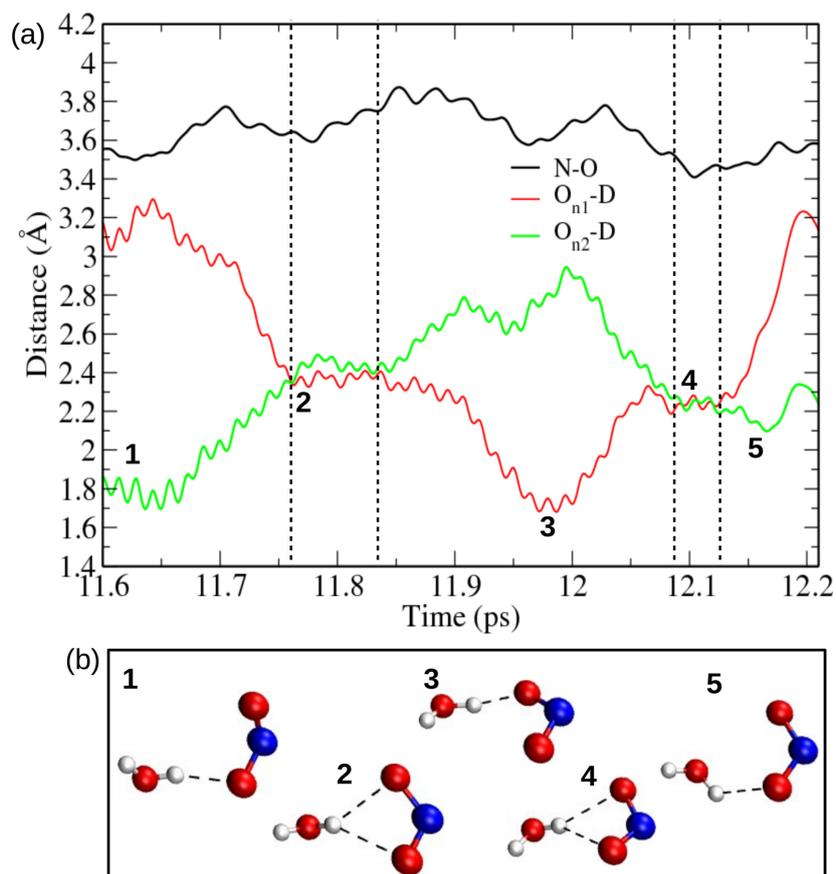


Fig.S7. (a) Fluctuating distances of the oxygen and deuterium atoms of selected water from the nitrogen and oxygen atoms of the nitrite ion for switching events of a hydrogen bond from D-O<sub>n2</sub> to D-O<sub>n1</sub> and then from D-O<sub>n1</sub> to D-O<sub>n2</sub> for an arbitrarily chosen trajectory segment. The deuterium atom of the selected water is found to remain weakly hydrogen bonded to both oxygens of the nitrite ion for short periods which are shown by vertical dashed lines. (b) Some representative configurations during the exchange event are shown.